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(54) Titania-Tantala-Silica interference filters and lamps using same

Interferenzfilter aus Titan-, Tantal- und Siliziumoxyd und Lampen mit diesem Filter

Filtres interférentiels en oxyde de titane, oxyde de tantale et oxyde de silicium et lampes utilisant de tels filtres

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(56) References cited:
EP-A- 0 300 579 **GB-A- 2 128 805**

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Description

This invention relates to optical interference filters which include alternating layers of tantala and silica and their use on lamps.

Thin film optical coatings known as interference filters which comprise alternating layers of two or more materials of different indices of refraction are well known to those skilled in the art. Such optical coatings are used to selectively reflect or transmit light radiation from various portions of the electromagnetic spectrum and are used in the lamp industry to coat reflectors and lamp envelopes.

Interference filters to be used for applications where the filters will be exposed to high temperatures in excess of about 500°C have been made of alternating layers of tantala (tantalum pentoxide, Ta_2O_5) and silica (SiO_2), wherein the silica is the low refractive index material and the tantala is the high refractive index material. Such filters and lamps employing same are disclosed, for example, in U.S. Patent Nos. 4,949,005; 4,689,519; 4,663,557; and 4,588,923.

The problem of severe stress formation associated with the use of interference filters consisting of alternating layers of silica and tantala when employed at high temperatures was recognized in U.S. Patent No. 4,734,614. This patent teaches that tantala has limited physical and chemical stability, and crystallizes to a polycrystalline form after about 30 minutes at 800°C which produces stress cracks visible as craquelé. This results in a filter that scatters both visible and infrared radiation, thereby rendering it unsuitable for its intended purpose.

Responsive to the need for a process which would apply a relatively uniform coating to a complex shape and which would not result in a film containing such stresses that the film cracks and peels off the substrate, U.S. Patent No. 4,949,005 to coinventor herein, T. Parham et al., provides an interference filter thin film optical coating consisting essentially of alternating layers of tantala and silica having relatively low light scattering which is suitable for use at high temperatures. The coatings are obtained by employing a chemical vapor deposition (CVD) process and, preferably, a low pressure chemical vapor deposition (LPCVD) process to produce the coatings on a suitable substrate, such as quartz. After application of the alternating layers, the optical filter produced is annealed to avoid catastrophic extrinsic stress formation from volume changes due to crystallization of tantala at temperatures above about 600°C which cause cracking and buckling, and result in poor adhesion, peeling, and undesirable optical scattering of light. Thus, the coated substrate must be heated to a temperature of between about 550 to 675°C, and held within this temperature range for a period of from about 0.5 to 5 hours.

Despite advances in the art, however, the need to anneal subsequent to deposition in order to reduce stress continues to be mandatory and increases the cost and time required for manufacturing interference filters and articles, such as lamps, including these interference filters.

Accordingly, it is an object of the present invention to provide an optical interference filter which includes alternating layers of tantala and silica in which the extrinsic stress of the tantala layer is reduced so that the need for post-deposition annealing is reduced and, when combined with an annealing treatment, for example, to relieve stress in the silica layers, produces filters having reduced stress-related damage.

It is another object of the present invention to provide a low stress optical interference filter which includes tantala and silica layers produced by a CVD or LPCVD process.

It is yet another object of the present invention to provide a lamp including a low stress optical interference filter which includes tantala and silica layers so that the energy efficiency of the lamp is improved.

These and other objects are accomplished by providing an optical interference filter, comprising a vitreous, light transmissive substrate containing a plurality of alternating layers of titania, tantala and silica in which at least some of said tantala layers are in contact with a corresponding titania layer and wherein each titania layer has a thickness less than that of the tantala layer it is in contact with.

Contacting a tantala layer with titania layers is effective to control the micro-structure of the tantala layer during subsequent crystallization by heating of the film and to thereby reduce extrinsic stress in the tantala layers.

The present invention additionally provides an electric lamp, comprising a light transmissive vitreous envelope enclosing an electric light source; and an optical interference filter according to the invention as described in the foregoing.

The interference filters according to the present invention are preferably provided by a CVD process, most preferably by an LPCVD process, the process comprising depositing a plurality of alternating layers of tantala and silica on a vitreous, light transmissive substrate by CVD, preferably LPCVD, from respective precursors to form a coated substrate. The process includes depositing a titania layer before or after deposition of at least some tantala layers. If an optical interference filter according to the invention is to be used at a temperature exceeding 650°C, it is preferable to anneal the coated substrate for a time and at a temperature effective to crystallize the tantala. Most preferably the coated substrate is held at a temperature ranging from about 550 to about 800°C for at least about one hour whereby the tantala crystallizes. Most preferably the coated substrate is held at about 650°C for about two hours. At a temperature ranging from about 650 to about 675°C, the tantala crystallizes within about one to two hours after which no further crystallization occurs even with prolonged heating.

Embodiments of the invention will now be described, by way of example, with reference to the accompanying drawings, in which:-

Figure 1 is a side view of an elongated tungsten halogen lamp having an optical interference film according to the present invention provided on its outer surface;

Figure 2 is an SEM photograph of a tantalum film with a titania pre-layer according to the invention at 7,000x magnification;

Figure 3 is an SEM photograph of a tantalum film with no titania pre-layer at 7,000x magnification for comparison with Figure 2; and

Figure 4 is a computed reflectance spectrum of a tantalum/silica IR reflecting filter with titania pre-layers according to the present invention.

The total stress of the optical interference film is the sum of three independent stresses, namely, thermal stress, intrinsic stress, and extrinsic stress. Thermal stress is a fixed stress that results from the thermal expansion mismatch between the substrate and the film. Intrinsic and extrinsic stresses are process dependent. Intrinsic stress arises from disorder in bond lengths and angles during film deposition. Extrinsic stress results from the crystallization of a previously amorphous material which produces a volume change, for example, crystallization of tantalum from amorphous tantalum at temperatures above about 600°C. The volume change during crystallization produces extrinsic stress which causes film cracking and buckling which produces sites for undesirable optical scattering of light and reduces the strength of the substrate.

The invention provides tantalum layers in optical interference filters having reduced extrinsic stress by providing tantalum in contact with a titania layer as a pre-layer and/or as a post-layer. Thus, subsequent crystallization of the amorphous tantalum layers in filters according to the invention results in a much more highly ordered crystalline tantalum than would otherwise be obtained. The tantalum layers according to the invention have finer grain structures and less microcracking, and the inventive methods and optical interference filters produced by these methods have reduced optical losses due to optical scattering.

Improved tantalum microstructure is obtained by providing a thin layer of titania adjacent to the tantalum layer. Thus, a pre-layer of tantalum may be deposited onto a thin layer of titania, and/or a thin titania post-layer may be deposited onto a layer of tantalum. For example, a pre-layer of titania having a thickness of about 130 Å was deposited by CVD from titanium ethoxide followed by deposition of tantalum thereover. The titania deposited in such a manner was found to be composed of extremely small microcrystallites of anatase having a size of about 300 Å.

It has been found that the use of an adjacent layer of titania in contact with an amorphous layer of tantalum is effective to nucleate a finer grain structure in the tantalum when the tantalum is later crystallized. This result was confirmed by an SEM study of such a titania/ tantalum bilayer and showed a remarkable transformation in the microstructure of the crystallized tantalum. The crystallized tantalum was composed of very small grains ranging in size from about 0.3 to 0.6 microns. The XRD pattern showed that this tantalum had essentially the same advantageous structure after crystallization as a tantalum layer doped with 1 mole % titania. That is, the tantalum was crystallized in a highly ordered manner. These advantageous results, moreover, continued even when the bilayers were heated to lamp operating temperatures ranging between about 650-900°C.

The adjacent titania layer, moreover, should be substantially thinner than the tantalum layer. By way of example but not limitation, the tantalum layer will generally be at least about 500 Å thick, whereas the pre-deposited and/or post-deposited titania layer contacting the tantalum layer will generally range from between about 50-150 Å thick. Of course there may be exceptions where the tantalum will be less than 500 Å, but the goal is to keep the titania layer thin enough to obtain the desired morphology when the tantalum subsequently crystallizes, while not being so thick as to unduly interfere with optical properties and make the film design unduly complex. This is because titania has a high coefficient of thermal expansion which results in thermal stress. Moreover, when single layers of titania are heated above about 900°C, conversion from anatase to rutile titania occurs and the film becomes hazy.

Turning now to the drawings, Figure 1 illustrates a lamp the outer surface of which is provided with a titania-tantalum-silica interference filter according to the present invention which reflects infrared radiation back to the filament where it is converted into visible radiation. This lamp is illustrative but is not intended to limit the present invention.

The lamp illustrated in Figure 1 comprises envelope 10 made out of a vitreous, light transmissive material capable of withstanding high temperatures of at least about 800°C, such as quartz. Each end of envelope 10 has a pinch seal portion 12 through which is sealed an inlead connector 13 electrically and mechanically attached by suitable means, such as welding, to molybdenum foil 14 which is hermetically sealed and embedded in the pinch seal portion 12 of the lamp. Leads 15 made out of a suitable refractory metal, such as molybdenum or tungsten, are attached to the other end of molybdenum foils 14 at one end and at the other end are connected to tungsten filament 17 which is supported on its axis within the envelope by a plurality of suitable supporting members 18, such as tungsten spiral wire supports of the type disclosed in U.S. Patent No. 3,168,670. Thin film optical interference filter 20 of the present invention is

provided on the outer surface of the lamp as a continuous coating.

Film 20 consists of alternating layers of tantala and silica arranged so as to adjust the pass-band and the stop-band characteristics of the emitted radiation of the lamp. The tantala layers are adjacent a titania pre-layer and/or post-layer according to the invention. The total number of combined layers of silica and tantala is ideally as large as possible to obtain maximum optical performance, however, stress considerations must be balanced with optical performance. The total number therefore preferably ranges from 8 to 100. Stress considerations become a factor as 20 layers are reached, particularly as 60 layers are reached.

In one embodiment, interference film 20 will reflect the infrared radiation emitted by tungsten filament 17 back to the filament, while transmitting the visible radiation. Alternatively, the interference film comprising the alternating layers of tantala and silica may be designed in the known manner to reflect visible radiation while transmitting infrared radiation. In yet another embodiment, film 20 can be designed so as to transmit radiation within a particular region of the electromagnetic spectrum, while reflecting that light which it is desired not be transmitted.

Figures 2 and 3 are SEM photographs which show tantala layers with and without an adjacent titania layer. These layers were prepared by an LPCVD process using tantalum ethoxide and titanium ethoxide or titanium isobutoxide.

Figure 2 shows a tantala film provided on a titania pre-layer at 7,000x magnification. The titania pre-layer had a thickness of 130 Å and the total film thickness was 3,800 Å. The sample was rapidly heated to 850°C in air and was held at that temperature for 24 hours as a torture test.

Figure 3 shows a tantala film without any titania pre-layer at 7,000x magnification. The tantala film had a thickness of 2,900 Å and was made for comparison with Figure 2. Cracking and buckling is seen. A comparison of Figures 2 and 3 clearly shows the provision of a titania pre-layer according to the invention advantageously resulted in much smaller crystallinity in the adjacent tantala layer compared to the tantala layer which didn't have an adjacent titania layer.

X-ray diffraction (XRD) studies of tantala layers produced according to the invention showed broad peaks of low intensity despite a grain structure having crystallites of 1-2 µm in size. This broadening in the XRD pattern is believed to be due to internal stresses in the film and/or crystalline imperfections, both of which are undesirable in films for optical applications. They create a weaker film having a greater tendency to separate at grain boundaries. Such films apply more stress to the substrate, increasing spallation and lifting of the film from the substrate. Both lifting and spallation of the film undesirably reduce the optical reflectance of the film and increase optical scattering.

A severe test for spallation for single layer tantala films and for multilayer tantala/silica films is to rapidly heat same above 800°C. The resulting film crack pattern of such rapidly heated samples was observed using scanning electron microscopy (SEM). The so-produced cracking/lifting of tantala results from the nucleation and growth of crystalline tantala from the amorphous phase. SEM studies of pure tantala layers showed film cracking and lifting of the cracked edges away from the quartz substrate. The deposition of tantala over a 130 Å titania film dramatically eliminates film cracking/lifting upon crystallization of tantala as shown in Figure 2. The titania layer is composed of sub-micron grains of anatase. The grain size of the tantala film (with titania pre-layer) is sub-micron and, as set forth above, it is reduced by a factor of about 3, i.e., from 1-2 µm to 0.3-0.6 µm, compared to an undoped tantala layer crystallized without an adjacent titania layer as shown in Figure 3. The reduction in grain size makes it apparent that the titania layer enhances the nucleation frequency of tantala grains. In summary, therefore, film cracking and lifting can be controlled by depositing tantala over or under a thin titania layer having a thickness ranging from about 50 to about 500 Å, preferably from about 50 to about 150 Å.

Figure 4 is a computed reflectance spectrum of a further example of an interference filter according to the present invention. The interference filter is a tantala/silica IR reflecting filter with titania pre-layers and has a total of 35 layers. FILM*STAR™ software for multilayer optical coatings was employed starting with a conventional 24 layer design interference filter having alternating layers of tantala and silica (12 layers of each), most of the tantala layers being preceded by and in contact with a thin layer of titania. The tantala film thicknesses were reduced in view of the titania layers and the design was reoptimized. In this particular design it was found advantageous to omit a titania layer before tantala layer 28.

As mentioned in U.S. Patent No. 5,138,219, column 7, lines 53-63, there are a large number of computer programs commercially available for optimizing multilayer coatings and one such list of some fifteen vendors and programs may be found on page 144 of the September, 1988 issue of PHOTONICS SPECTRA magazine, an optics industry trade journal. Included in this list as illustrative, but nonlimiting examples, are CAMS which is available from Optikos located at 143 Albany Street, Cambridge, MA 02139, and FILM*STAR™ available from FTG Software Associates at P.O. Box 579, Princeton, NJ 08524.

The following is a list of the 35 layers of the interference filter of Figure 4. The high refractive index material, H, is tantala having a refractive index of about 2.19; the low refractive index material, L, is silica having a refractive index of about 1.45; and layers, T, are thin layers of titania having a refractive index of 2.54. Refractive indices were determined at 600 µm.

1	110.0 T	14	1137.7 H	27	1801.5 L
2	917.8 H	15	1987.2 L	28	2386.3 H
3	1737.4 L	16	110.0 T	29	1801.5 L
4	110.0 T	17	1137.7 H	30	110.0 T
5	917.8 H	18	1987.2 L	31	2279.6 H
6	1737.4 L	19	110.0 T	32	1801.5 L
7	110.0 T	20	1137.7 H	33	110.0 T
8	917.8 H	21	1987.2 L	34	2197.4 H
9	1737.4 L	22	110.0 T	35	804.7 L
10	110.0 T	23	1137.7 H		
11	917.8 H	24	1987.2 L		
12	1737.4 L	25	110.0 T		
13	110.0 T	26	2279.6 H		

The interference filter thin film optical coatings of the present invention can be prepared by any of a variety of methods including thermal evaporation, sputtering, solution deposition techniques, such as dip coating, and CVD. As set forth in the foregoing, however, the interference filter thin film optical coatings of the present invention are preferably prepared by a CVD process and, most preferably, by an LPCVD process wherein a suitable metal oxide precursor reagent or reagents for each material of the film is separately introduced into a decomposition chamber wherein it is decomposed or reacted to form the metal oxide on a heated substrate.

The LPCVD process permits application of these coatings onto surfaces having a complex shape and provides good control of thickness. Separate layers of silica and tantalum (and titania when employed) are applied onto the substrate in this fashion until the desired filter design is achieved. Such chemical vapor deposition techniques are well known to those skilled in the art and are disclosed in, for example, U.S. Patent Nos. 4,006,481; 4,211,803; 4,393,097; 4,435,445; 4,508,054; 4,565,747; and 4,775,203.

In forming the metal oxide films on a substrate in accordance with the present invention, the substrate is positioned within a deposition chamber. The chamber is generally contained within a furnace so that the substrate reaches the desired temperature to achieve the reaction or decomposition and concomitant deposition of the metal oxide film on the substrate. These temperatures will generally range between about 350 to 600°C, depending upon the particular reagents used.

For an LPCVD process, the deposition chamber is evacuated and a suitable organometallic precursor of the desired metal oxide in the vapor state is permitted to flow through the deposition chamber by any suitable means. When the reagent flows into the deposition chamber it is decomposed to deposit a metal oxide film on the substrate. When the desired film thickness is achieved the reagent flow is stopped, the chamber evacuated and the reagent for another material is flowed into the deposition chamber until the desired thickness of that material is achieved. The process is repeated until the desired multiple layer interference filter is formed.

Illustrative, but non-limiting examples of compounds suitable for use in the present invention for depositing a silica film by CVD or LPCVD include diacetoxysilane, tetraacetoxysilane, and silicon tetrakis diethoxyamine. Suitable reagents for use in the present invention for depositing a film of tantalum by CVD or LPCVD include tantalum methoxide, tantalum pentaethoxide, tantalum isopropoxide, tantalum butoxide, mixed tantalum alkoxides, and tantalum pentachloride and water and/or oxygen. Suitable reagents for use in the present invention for depositing a film of titania by CVD or LPCVD include titanium methoxide, titanium ethoxide, titanium propoxide, titanium isopropoxide, titanium butoxide, titanium isobutoxide, and mixed titanium alkoxides.

No carrier gas is required in the deposition chamber to facilitate movement of the reagent(s) through the chamber, although an inert carrier gas can also be employed, if desired as is known in the art. The pressure in the chamber during the deposition process will, in general, range between about 0.1 to 5.0 torr, depending upon the reagent used and the temperature of the substrate. Atmospheric pressure may be employed for a CVD process. The flow rate of the gaseous reagent in the deposition chamber will generally range between about 10-50,000 SCCM, depending upon the size of the reaction chamber, the reagent, presence of a carrier gas and desired rate of deposition, etc..

Individual layers of metal oxide can be uniformly deposited employing this process and layers having a uniformity of film thickness within plus or minus about 2% have been successfully deposited on both flat and curved substrates. Uniform films of tantalum, titania, and silica can be formed ranging from about 100 to about 20,000 Å in thickness.

In forming the alternating layers of silica, tantalum and titania of the interference filter of the present invention, a layer of tantalum or silica will first be deposited and flow of the particular silica or tantalum reagent to the chamber will be stopped, the chamber evacuated, and then flow of the reagent which is a precursor or reactant for another film will be

introduced into the chamber. The process is repeated until the desired number of layers for the interference filter have been formed.

while not wishing to be held to any particular theory, it is believed heating interference filters according to the invention within the temperature range of 550 to 800°C results in crystallization of the tantala layers to form a great number of tantala crystallites without significant growth of the individual crystallites and the concomitant formation of the catastrophic stress that results from such crystal growth. Preferably the temperature will be between about 650 to about 675°C, because at temperatures below about 600°C, crystallite formation generally takes an excessively long time and not be commercially feasible. The tantala layer, as deposited by CVD or LPCVD at a temperature of 350 to 550°C, is amorphous and the subsequent heat treatment at 550 to 800°C is believed to permit the formation of crystallites in an amount sufficient to avoid the formation of the catastrophic stress resulting from the anisotropic growth of the orthorhombic tantala crystallites. The present invention reduces the need for an annealing treatment and, when combined with an annealing treatment, for example, to relieve stress in the silica layers, produces filters with less cracking, lifting, spalling and other stress-related damage.

Claims

1. An optical interference filter, comprising a vitreous, light transmissive substrate containing a plurality of alternating layers of titania, tantala and silica in which at least some of said tantala layers are in contact with a corresponding titania layer and wherein each titania layer has a thickness less than that of the tantala layer it is in contact with.
2. An optical interference filter according to claim 1 wherein said tantala is crystalline.
3. An electric lamp, comprising a light transmissive vitreous envelope enclosing an electric light source with an optical interference filter produced on said vitreous envelope comprising a plurality of alternating layers of titania, tantala and silica in which at least some of said tantala layers are in contact with corresponding titania layers and wherein each titania layer has a thickness less than that of the tantala layer it is in contact with.

Patentansprüche

1. Optischer Interferenzfilter, umfassend ein glasartiges, lichtdurchlässiges Substrat, das eine Vielzahl abwechselnder Schichten aus Titanoxid, Tantaloxid und Siliciumoxid enthält, wobei sich mindestens einige der Tantaloxid-Schichten in Kontakt mit einer entsprechenden Titanoxid-Schicht befinden, und wobei jede Titanoxid-Schicht eine geringere Dicke hat als die Tantaloxid-Schicht, mit der sie sich in Kontakt befindet.
2. Optischer Interferenzfilter nach Anspruch 1, worin das Tantaloxid kristallin ist.
3. Elektrische Lampe, umfassend einen lichtdurchlässigen, glasartigen Kolben, der eine elektrische Lichtquelle einschließt, wobei ein optischer Interferenzfilter auf dem Glaskolben hergestellt ist, der eine Vielzahl abwechselnder Schichten von Titanoxid, Tantaloxid und Siliciumoxid umfaßt, wobei mindestens einige der Tantaloxid-Schichten sich in Kontakt mit entsprechenden Titanoxid-Schicht befinden, und wobei jede Titanoxid-Schicht eine geringere Dicke hat als die Tantaloxid-Schicht, mit der sie sich in Kontakt befindet.

Revendications

1. Filtre optique interférentiel, comprenant un substrat vitreux, transparent à la lumière, qui contient une pluralité de couches alternées d'oxyde de titane, d'oxyde de tantale et de silice, dans lequel certaines au moins desdites couches d'oxyde de tantale sont en contact avec une couche correspondante d'oxyde de titane et dans lequel chaque couche d'oxyde de titane a une épaisseur inférieure à celle de la couche de tantale qui est en contact avec elle.
2. Filtre optique interférentiel selon la revendication 1, dans lequel ledit oxyde de tantale a une structure cristalline.
3. Lampe électrique comprenant une enveloppe vitreuse, transparente à la lumière, qui renferme une source électrique de lumière, avec un filtre optique interférentiel formé sur ladite enveloppe vitreuse, qui comprend une pluralité de couches alternées d'oxyde de titane, d'oxyde de tantale et de silice, dans lequel certaines au moins desdites

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couches d'oxyde de tantale sont en contact avec des couches correspondantes d'oxyde de titane et dans lequel chaque couche d'oxyde de titane a une épaisseur inférieure à celle de la couche de tantale qui est en contact avec elle.

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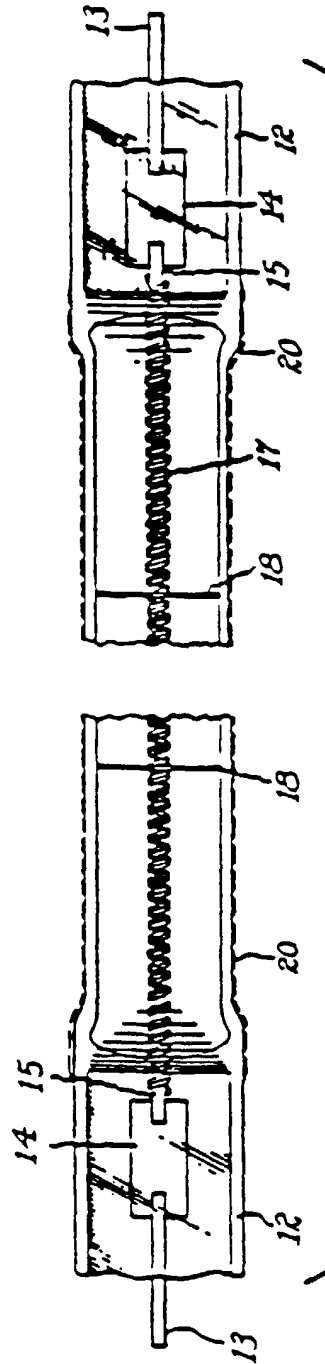


Fig. 1

FIG. 3



FIG. 2

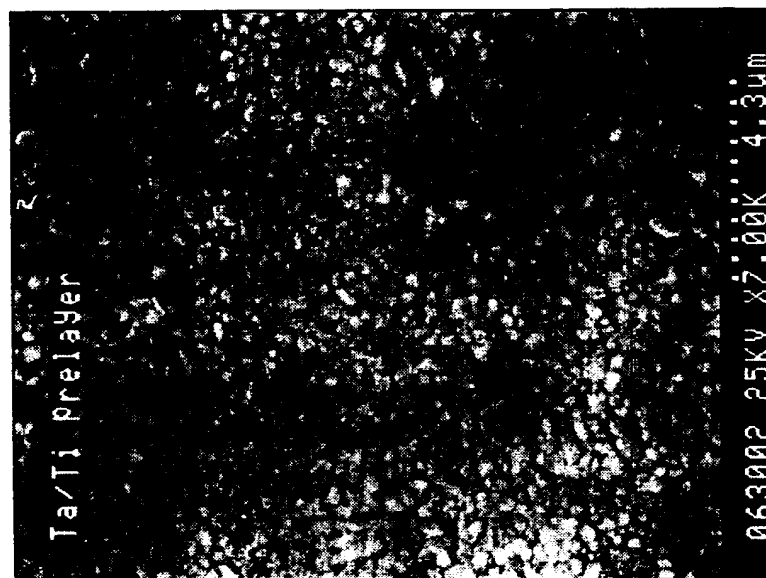


FIG. 5



FIG. 4

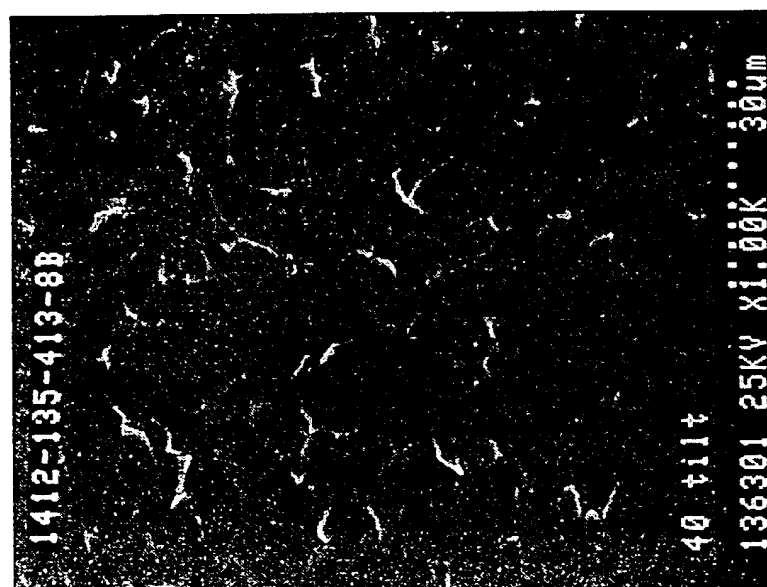
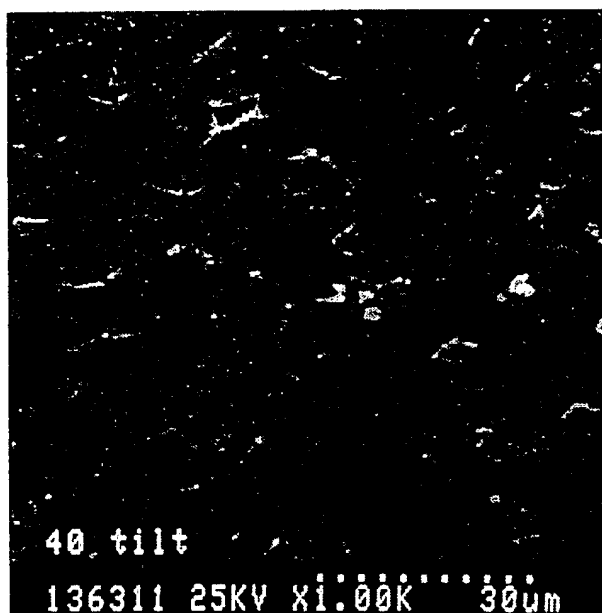


FIG. 6



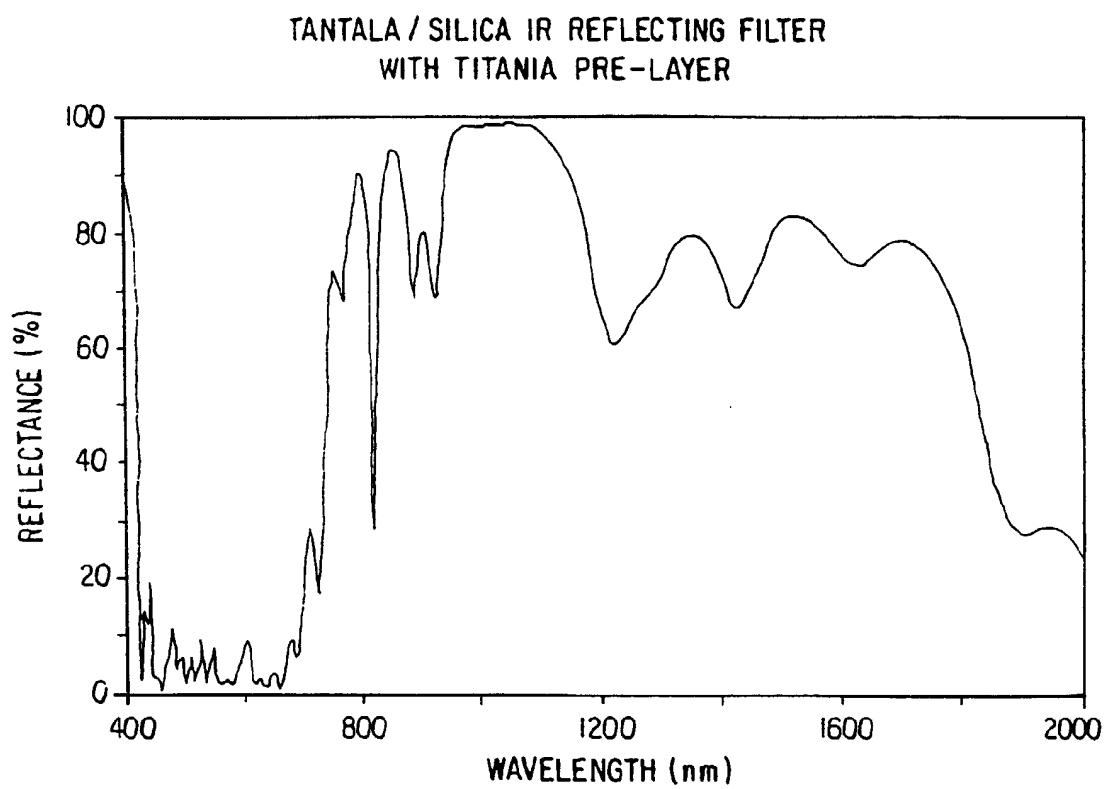


FIG. 7